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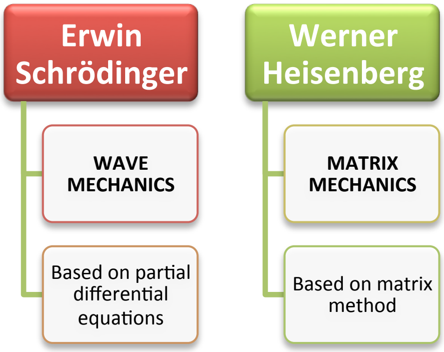
1. Learning Outcomes

After studying this module, you shall be able to:

- Know the basic equation of Quantum Mechanics.
- Learn the two forms of Schrödinger equation.
- Identify the steps involved in studying a system quantum mechanically.
- Write Schrödinger equation for a chemical system.

2. Formulation of Quantum Mechanics

Classical mechanics failed to correctly explain the experimental behavior of various phenomena such as Blackbody Radiation, Photoelectric Effect, Compton Effect, Atomic Spectrum, Heat Capacity of Solids and so forth. It was established latter that the above mentioned phenomena could be correctly reproduced by considering particle behavior (energy quantization $E = h\nu$) of radiation. Louis De Broglie in 1924 said that nature manifests itself in two forms – matter and radiation. And if radiation has dual behavior [wave (reflection, refraction, diffraction, etc.) and particle, with energy $E = h\nu$ (photoelectric effect, Compton effect, etc.], then by virtue of symmetry, matter should also have dual behavior. Broglie suggested that particles have wave-like properties characterized by a wavelength ($\lambda = h/p$ where $p = mv$). This idea inspired Schrödinger and Heisenberg; and they independently formulated quantum theory in 1925, to study the behavior of microscopic matter.



At first sight, the two approaches appear different but, later Dirac and Newman showed that in essence the two formulations are mathematically equivalent.

In this paper, we will be discussing the detailed theory and application of Schrödinger Quantum Mechanics (since it appears more familiar to chemists than Heisenberg formulation).

3. Schrödinger Quantum Mechanics

The Schrödinger's formulation of quantum theory revolves around a partial differential equation now popularly known as the Schrödinger equation. Schrödinger formulated non-relativistic quantum mechanics (where mass is assumed to be constant and does not vary with velocity/speed). Whereas, Dirac developed relativistic quantum theory (where mass varies with velocity/speed).

The Nobel Prize in Physics 1933 was awarded jointly to Erwin Schrödinger and Paul Adrien Maurice Dirac.

Over here, we will restrict our discussions to Schrödinger's non-relativistic quantum mechanics. The Schrödinger equation describes the behavior of atomic particles by means of a function called the wave-function or state function ψ.

There are two forms of Schrödinger equation, a time-dependent and a time-independent. The wave-function is a function of particle's position and time, ψ(*x*,*y*,*z*,*t*), in the time-dependent Schrödinger equation, whereas it a function of position only, ψ(*x*,*y*,*z*), in the time-independent Schrödinger equation.

3.1 Time – dependent Schrödinger equation:

$$\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t}, \qquad where\ \hbar = \frac{h}{2\pi}$$

Here, $\hat{H}$ is the Hamiltonian operator, ψ is the wave-function, and h is the Planck's constant. This form of Schrödinger equation is used for non-conservative systems where energy changes with time (mainly used in spectroscopy). This form is not symmetrical in the sense that it is doubly differential with respect to position and singly differential with respect to time. This affects the continuity of the wave-function.

3.2 Time – independent Schrödinger equation:

The time-independent Schrödinger equation is used when dealing with stationary states (conservative systems) where energy of the system remains constant with respect to time.

$$\hat{H}\psi = E\psi$$

where $\hat{H}$ is the Hamiltonian operator, ψ is the wave-function and E is the energy of the state ψ.

Over here, we will be studying the time-independent Schrödinger equation which states that:

When the Hamiltonian $\hat{H}$ operator acts on the wave-function ψ, the result is proportional to the same wave-function ψ (stationary state) and the proportionality constant, E, is the energy of the state ψ.

In the time-independent Schrödinger equation, the Hamiltonian operator is equivalent to the total energy operator or one can say that it is the quantum mechanical operator of energy. It is taken as sum of kinetic energy operator ($\widehat{\boldsymbol{T}}$) and potential energy operator ($\widehat{\boldsymbol{V}}$).

$$\widehat{\boldsymbol{H}} = \widehat{\boldsymbol{T}} + \widehat{\boldsymbol{V}}$$

Operator is a mathematical command that tells you what to do on what follows. Operator must precede the function on which it acts. For every measureable observable/property, there is a corresponding operator.

Hamiltonian does not have any units. It is a mathematical command. It is dimensionless

4. Operations of quantum mechanics

To study a microscopic system quantum mechanically using the Schrödinger equation, the following four steps are mainly followed:

4.1 Writing Schrödinger equation for the system under consideration

Schrödinger equation (SE) is the fundamental equation of Quantum Mechanics. This equation has no derivation.

$\hat{H}\psi = E\psi \qquad (\widehat{cap})\ is\ used\ over\ operator$

$\hat{H} = Hamiltonian\ operator\ (an\ energy\ operator)$

$\psi = (psi) = wave - function\ or\ eigen\ function\ or\ state\ function$

$E = Total\ energy\ of\ the\ system$

No two systems have same Schrödinger equation i.e. Schrödinger equation differs from system to system in only $\hat{H}$.

$\hat{H}$ is equal to sum of Kinetic energy operator and Potential energy operator.

$\hat{H} = \hat{T} + \hat{V}$

$\hat{T} = Kinetic\ energy\ operator\ (it\ is\ never\ zero\ for\ a\ system)$

$\hat{V} = Potential\ energy\ operator\ (it\ may\ or\ may\ not\ be\ zero\ for\ a\ system)$

$Since \qquad \hat{H}\psi = E\psi$

Therefore, $(\hat{T} + \hat{V})\psi = E\psi$

Kinetic energy of a microscopic particle can never be zero as microscopic particles can never be at rest. This is a direct consequence of Heisenberg uncertainty.

$$\Delta x.\Delta p_x \geq \frac{h}{4\pi}$$

If particle is at rest, then its exact position is known, ⇒ $\Delta x = 0\ and\ \Delta p_x \rightarrow \infty or\ m\Delta v = \infty$ i.e., the particle has some kinetic energy ⇒ particle cannot be at rest.

Schrödinger equation for a single particle of mass m with zero potential energy, moving in one dimension (let's say *x* direction)

$$\hat{V} = 0$$

$$\hat{H}\psi = E\psi \Rightarrow \hat{T}\psi = E\psi$$

$$\hat{T} = \widehat{T_x} = \frac{-h^2}{8\pi^2 m}.\frac{d^2}{dx^2} \quad (Kinetic\ energy\ in\ x\ direction)$$

$$SE\ becomes \qquad \frac{-h^2}{8\pi^2 m}.\frac{d^2}{dx^2}\psi = E\psi$$

Now, suppose if the particle is moving in *xy* plane with zero potential energy, then the Schrödinger equation becomes

$$\hat{T} = \widehat{T_{xy}} = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\right]\psi = E\psi$$

If the particle is moving in space i.e., in three dimensions (*x,y,z*), then the Schrödinger equation becomes

$$\hat{T} = \widehat{T_{xyz}} = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

$$where \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = \nabla^2 (del\ square) = Laplacian\ operator$$

$$\left[\frac{-h^2}{8\pi^2 m}\nabla^2\right]\psi = E\psi \quad with\ \hat{V} = 0$$

$$If\ \hat{V} \neq 0, then\ SE\ becomes \left[\frac{-h^2}{8\pi^2 m}\nabla^2 + \hat{V}\right]\psi = E\psi$$

So, for “N” particle system moving in 3 dimensional space, the Schrödinger equation becomes

$$\left[\frac{-h^2}{8\pi^2}\sum_{i=1}^{N}\frac{\nabla_i^2}{m_i}+\hat{V}\right]\psi = E\psi$$

Where there are N kinetic energy terms for N particles and one total potential energy term for the system under consideration.

Schrödinger equation for a linear harmonic oscillator

Potential Energy of linear harmonic oscillator is given by:

$$\hat{V}=\frac{1}{2}kx^2 \qquad \hat{T}=\frac{-h^2}{8\pi^2 m}\cdot\frac{d^2}{dx^2}$$

$$\textit{SE becomes} \qquad \left(\frac{-h^2}{8\pi^2 m}\cdot\frac{d^2}{dx^2}+\frac{1}{2}kx^2\right)\psi = E\psi$$

4.2 Defining Boundary Conditions for the system

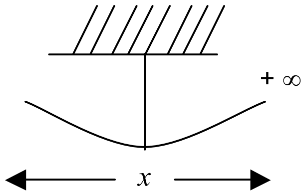
Boundary conditions means restrictions on the system such as dimensions of the system or radius of an atom.

- Particle in 1-D Box

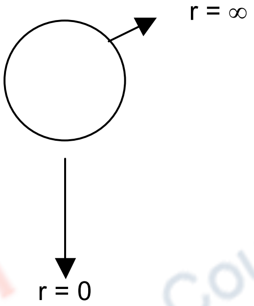
In 1-D box, x cannot be less than zero or greater than L

- Oscillator

The amplitude of the oscillator is in between -∞ to +∞



- Electron in an atom
  (Radius of the atom, r)
  r = 0 and r = ∞ are two boundaries



This step is essential because a well behaved wave-function, ψ must satisfy boundary conditions.

4.3 Solution of Schrödinger equation

This step is the most difficult and time consuming step in studying a system quantum mechanically.

Once the Schrodinger equation has been written and boundary conditions are known, then it is solved to obtain ψ and E. ψ must always satisfy boundary conditions.

Wave-function ψ (also called state function or eigen function) is the store house of information. The entire information of the system is contained in ψ.

4.4 Extracting information out of ψ

From ψ the properties which exist for a system can be found out. The properties of the system can be determined using certain rules of Quantum Mechanics:

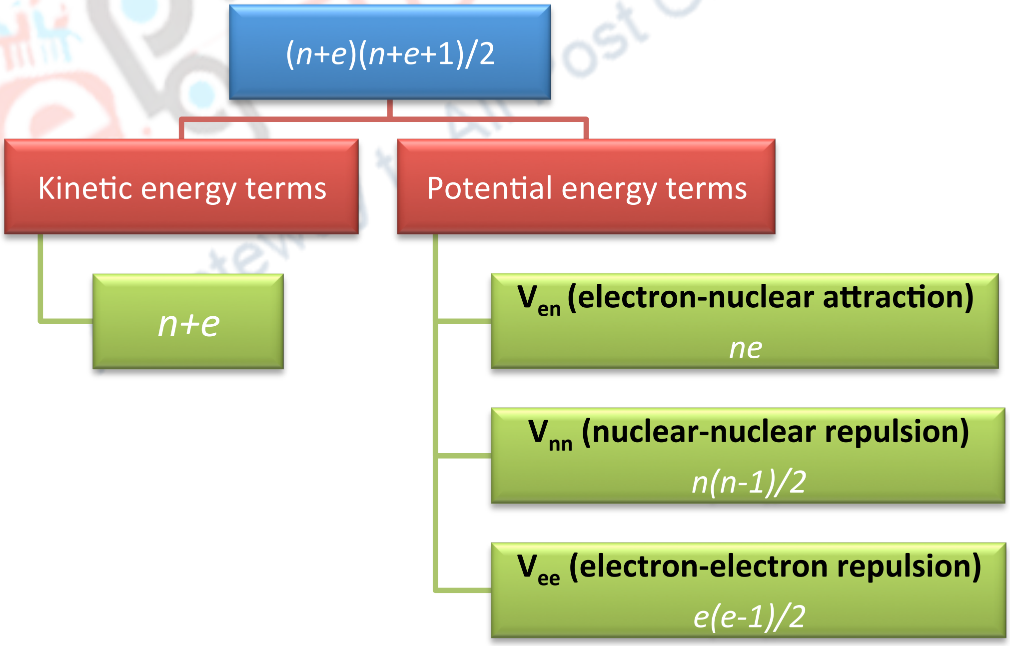
(1) Eigen value equation (2) Mean value Theorem

The details will be discussed in subsequent modules.

5. Writing Schrödinger equation for chemical system

For a given chemical system with "n" nuclei and "e" electrons the total number of terms (kinetic energy and potential energy terms) in Hamiltonian can be calculated using the formula given below:

$$Number\ of\ \hat{H}\ terms = \frac{(n+e)(n+e+1)}{2}$$



The following table shows the number of terms involved in some of the chemical systems:

System	***n***	***e***	**$(n+e)(n+e+1)/2$**
H	1	1	3
He^+	1	1	3
He	1	2	6
He_2	2	4	21
C	1	6	28
CH_4	5	10	120
C_6H_6	12	42	1485

6. Summary

- Rather than saying that a particle has a specified position and momentum, we instead describe it by a wave-function, ψ which is a function of all the coordinates of the particle and of time.

$$\boldsymbol{\psi = \psi(x, y, z, t)}$$

- Wave-function ψ (also called state function or eigen function) is the store house of information. The entire information of the system is contained in ψ.
- The Schrödinger's formulation of quantum theory revolves around a partial differential equation now popularly known as the Schrödinger equation. Over here, we have considered time-independent Schrödinger equation.

$$\boldsymbol{\hat{H}\psi = E\psi}$$

- Hamiltonian operator, $\boldsymbol{\hat{H}}$ is equal to sum of Kinetic energy operator and Potential energy operator.

$$\boldsymbol{\hat{H} = \hat{T} + \hat{V}}$$

- Operation of quantum mechanics consists of four steps:
  1. Writing Schrodinger equation for the system under consideration
  2. Defining Boundary Conditions for the system
  3. Solution of Schrodinger equation
  4. Extracting information out of ψ

- The number of terms in Hamiltonian for a chemical system with "*n*" nuclei and "*e*" electrons can be calculated using the formula given below:

$$Number\ of\ \hat{H}\ terms = \frac{(n+e)(n+e+1)}{2}$$